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ABSTRACT

This document is an instructional module package prepared in objective form for use by an instructor familiar with fluoride analysis procedures. Included are objectives, an instructor guide, student handouts, and a list of reference material. This module considers the determination of fluoride in water supplies using the SPANDS and electrode analytical methods. (Author/RH)

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FLUORIDE ANALYSIS

Training Module 5.200.2.77

Prepared for the

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September, 1977

SE 024 155

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Module No:	Module Title: Fluoride Analysis
Approx. Time:	Topics: 1. Introduction 2. SPANDS Method 3. Electrode Method 4. Summary

Objectives:

Upon completion of this module the participant should be able to:

1. Conduct a fluoride analysis using the SPANDS method on the electrode method and properly translate the raw data from the test into proper units of expression.
2. Compare and contract the methods for fluoride analysis.

Instructional Aids:

Handout
Overheads
EPA video tape: Determination of Fluoride in Water by J. Ptaft.

Instructional Approach:

Lecture
Lab

References:

Standard Methods, 14th Edition
Fluoride Determinations in Water
USEPA Water Supply Programs Division

Class Assignments:

None

Instructional Aids

EPA slide-tape is available from:

Eileen Hopewell
National Training Center
Water Programs Operation
Vine & St. Claire St.
Cincinnati, Ohio 45268

Overheads

Typed overheads are an example of overhead layout and content. For classroom use the overhead should be constructed using colored, 1/4 inch dry transfer letters.

Other overheads may be copied directly.

Handouts

Handouts may be copied directly. Section 6 and Section 9.

Lab supplies and apparatus

Supplies and apparatus should be supplied per handouts so that participants may work in groups of 2 or 3.

Module No:	Module Title: Fluoride Analysis
	Submodule Title:
Approx. Time:	Topic: Introduction

Objectives:

Upon completion of this module, the participant should be able to:

1. Identify the standard methods for fluoride analysis.
2. Indicate why a visual comparator cannot be used in the SPANDS Methods.
3. List interferences to the SPANDS Method and electrode method.

Instructional Aids:

Handout Chemistry of Fluoride Analysis

Instructional Approach:

Lecture

References:

See Handout

Class Assignments:

Module No:	Topic: Introduction

Instructor Notes:	Instructor Outline:
Handout Pages 13 - 23 Note: Scott-Sanchis method no longer a Standard Method	1. a. List the analytical methods for fluoride b. Indicate the standard methods SPADNS Electrode 2. a. Discuss the color change from deep red to light red b. Indicate that it is a small change c. Indicate that our eyes cannot detect the change 3. a. Discuss sources of error in the SPANDS method b. Discuss sources of error in the electrode method c. Indicate methods of control and distillation procedure

Module No:	Module Title: Fluoride Analysis
	Submodule Title:
Approx. Time:	Topic: SPANDS Method

Objectives:

Upon completion of this module, the participant should be able to:

1. Identify the proper apparatus and reagents needed for the SPANDS Method.
2. Conduct a fluoride analysis using the SPANDS Method given proper equipment reagents and procedures sheet.
3. Translate the raw results from the test into proper units of expression.

Instructional Aids:

Handout
Lab equipment per handout
EPA video tape

Instructional Approach:

Lab

References:

Fluoride Determination in Water
Standard Methods, 14th Edition

Class Assignments:

Module No:	Topic: SPANDS Method

Instructor Notes:	Instructor Outline:
Handout Pages 29 - 32	1. a. List and identify the apparatus for the SPANDS Method. b. List and identify the reagents needed for the SPANDS Method c. Indicate source of supply d. Demonstrate the makeup of the reagents. 2. a. Demonstrate the SPANDS Method b. Have participants conduct a SPANDS fluoride analysis 3. a. Demonstrate the make of standard curves and the use of them to translate raw data into proper units of expression. b. Have participants translate their raw data into proper units of expression.

Module No:	Module Title: Fluoride Analysis
	Submodule Title:
Approx. Time:	Topic: Electrode Method

Objectives:

1. Identify the proper apparatus and reagents needed for the electrode method.
2. Conduct a fluoride analysis using the electrode method given proper equipment and reagents and procedures sheet.
3. Translate the raw results from the test into proper units of expression.

Instructional Aids:

Handout
Lab equipment per handout

Instructional Approach:

Lab

References:

Fluoride Determination in Water
Fluoride Electrode Instructions
Standard Methods, 14th Edition

Class Assignments:

Module No:	Module Title: Fluoride Analysis
	Submodule Title:
Approx. Time:	Topic: Summary

Objectives:

1. Compare and contrast the methods for fluoride analysis and select a method best suited for an individual plant.

Instructional Aids:

Handout

Instructional Approach:

Discussion

References:

Fluoride Determinations in Water

Class Assignments:

Module No:	Topic: Summary
Instructor Notes:	Instructor Outline:
	Compare and contrast the two methods. Discuss sources of error, cost reagents, speed of analysis control of interferring ions.

EVALUATION

T F There are two standard methods for fluoride, the SPADNS method and the Electrode method.

T F A color comparison may be used in place of the photometric type instrument in the SPADNS method.

T F A normal pH meter can be used with the Fluoride electrode.

T F In the SPANDS method the higher the fluoride concentration the lighter the red color becomes.

T F There are many non-standard methods for fluoride.

T F Chlorine will interfere with the SPANDS method and cause a positive error.

T F Aluminum, hexametaphosphate cause significant errors in the SPADNS method.

T F The electrode method has less interference problems than the SPADNS method.

Practical Evaluation

Determine the fluoride level in a given water sample with an accuracy of ± mg/l given proper equipment and procedures sheet. Participant may use the SPADNS method or the electrode method.

FLUORIDE: INTRODUCTION

Environmental Significance

The element fluorine does not occur free in nature, but exists only as fluoride in compounds found in volcanic gases and in certain minerals such as fluorspar, calcium fluoride, cryolite, and sodium aluminum fluoride. Fluoride is not common in natural waters, but in some areas the fluoride concentration of water may be as high as 10 mg/liter due to the leaching of fluoride-containing materials. Fluoride is toxic to aquatic life, particularly in concentrations over 1.5 mg/liter.

In sufficiently high doses, fluoride is toxic to humans. Doses of 250 to 450 mg may give symptoms of poisoning, while doses of 2.5 g may be fatal. Prolonged use of drinking water containing 4.0 to 5.0 mg fluoride/liter will cause mottling of tooth enamel, particularly in children, and prolonged use of drinking water with higher fluoride oncentrations may cause increased bone density, lessening motility. At lower concentrations, fluoride has the beneficial effect of lessening the occurrence of dental caries in children. When the fluoride concentration of drinking water is maintained at 1.0 mg/liter, the occurrence of dental caries may be reduced up to 50%. At this level, fluoride is not known to cause adverse psysiological effects.

Water Treatment

Addition of fluoride to water is usually necessary to obtain the ideal fluoride concentration for prevention of dental caries without causing adverse effects. In some instances, however fluoride removal may be necessary. Fluoridation of water requires careful control to insure that

the optimum level of fluoride is maintained so that the fluoridation procedure is both safe and effective. Defluoridation involves the removal of fluoride by percolation of water through activated aluminum or bone char, or by the settling of fluoride with magnesium compounds in settling basins.

Industrial Significance

Fluoride is used in bleaching, disinfecting, glass etching, and wood preservation. Cryolite is used in the manufacture of aluminum, and fluorspar is used as a flux in smelting and ceramics. Fluoride is not normally found in industrial wastes, however, except as the result of spillage.

Excessive fluoride concentration in a water supply may be harmful to certain industries such as the food, beverage, and pharmaceutical industries because fluoride may concentrate in the end product. For example, if corn is milled in water with a fluoride concentration of 1 mg/liter, the corn syrup produced may have a fluoride concentration of up to 5 mg/liter. A fluoride concentration of 1.0 mg/liter is considered acceptable for most industrial uses.

Methodology

The colorimetric method for the determination of fluoride is an inverse spectrophotometric procedure involving the reaction of fluoride with zirconium in a zirconium-dye lake. As zirconium is removed from the dye complex, a colorless complex (ArF_6) forms, resulting in a loss of color. Use of sodium 2-(parasulfophenylazo)-1, 8-dihydroxy-3, 6-napthalene disulfonate (SPANDS) in an acid solution allows the reaction between fluoride and zirconium to proceed very rapidly, eliminating the necessity of waiting for color change or for reading the loss in color while the reaction is still

proceeding. Increased transmittance of the sample is read at 580 nm. If a reagent blank is used to set the spectrophotometer to 35% T, the fluoride concentrations of interest fall in a convenient transmittance range for construction of a standard curve.

The SPANDS method may be applied to most water samples without distillation. However, certain interferences can only be removed by distillation from an acidic solution. These interferences include alkalinity over 5,000 mg/liter, chloride in concentrations greater than 7,000 mg/liter, aluminum greater than 0.1 mg/liter, iron greater than 10 mg/liter, phosphate in concentrations over 16 mg/liter, and sulfate in concentrations over 200 mg/liter. Color and turbidity also interfere. Chlorine in a sample must be removed by sodium arsenite prior to analysis.

Concentration Range

The U.S. Public Health Service drinking water standards specify a fluoride concentration based on the average maximum daily temperature. The theory is that in warmer climates children drink more water, and that fluoride concentration in water in warmer climates should, therefore, be lower. In a region where the average maximum daily temperature is 50.0 - 53.7° F the recommended optimum concentration is 1.2 mg F^-/liter with a maximum concentration of 1.7 mg F^-/liter. In regions where the average maximum temperature is 79.3 - 90.5° F, the recommended optimum is 0.7 mg F^-/liter and the maximum limit is 0.8 mg F^-/liter. The World Health Organization recommends fluoride drinking water standards of 1.5 mg/liter.

This SPANDS method is directly applicable to samples in the range of 0.05 to 2.0 mg F^-/liter.

CHEMISTRY OF FLUORIDE ANALYSIS

Analytical Methods

Because of the quantities of fluoride normally found in drinking water are so small, the analytical method must be adapted to the measurement of these quantities.

A. Gravimetric methods involve the precipitation of fluoride as part of a heavy complex, so that sufficient material can be obtained for accurate weighing.

B. Volumetric methods usually entail concentration of the sample so that the volume of titrant is large enough to be measured accurately. In addition, the color change of the indicator at the endpoint is extremely difficult to detect.

C. Other methods are available, such as polarographic and potentiometric, but these involve expensive and elaborate equipment, and furthermore are not well adapted to small quantities of fluoride.

D. Until recently, the best analytical methods for determining fluoride in water were the colorimetric methods, and two of those in Standard Methods belong to this category. The colorimetric methods are sensitive to minute quantities of fluoride and are easily performed with the simplest type of glassware and instruments.

E. The development of an electrode which is almost completely specific for fluoride ions has revolutionized the field of fluoride analysis. The electrode method is extremely sensitive and requires, in addition to the fluoride electrode itself, only an ordinary pH reference electrode and an ordinary pH reference electrode and an expanded-scale pH meter

(or digital meter) for the analysis of waters containing any likely concentration of fluoride.

The Colorimetric Reaction

The basis for two of the fluoride methods now listed in Standard Methods is the zirconium-dye reaction. In this reaction, a red lake is produced by the combination of dye and zirconium. Any fluoride present in the water sample removes zirconium from the reaction, thus decreasing the intensity of color present.

A. The visual Scott-Sanchis method uses alizarin as the dye. In water samples which are high in fluoride, the only color apparent is the yellow color of the unreacted dye. Conversely, in low fluoride samples, the color approaches the deep red of the zirconium-alizarin lake. Intermediate fluoride concentrations give colors which are intermediate between the two. The colors are all relatively pale and are adaptable for viewing through long Nessler tubes. The reaction is not an immediate one, but progresses with time. After one hour the reaction rate is extremely slow, and for this reason the time interval between adding reagent and making the measurement has been selected as 60 minutes. The reaction rate is affected by a number of factors, among them the acidity and temperature of the reaction mixture.

B. The photometric method used SPADNS as the dye. (SPADNS is an abbreviation of sodium 2-(p-sulfophenylazo)-1, 8-dihydroxy-3, 6 napthalene disulfonate). The color of the reaction mixture (water sample plus reagent) varies from very deep red in the absence of fluoride to light red when the concentration of fluoride is high. The change in

color caused by small changes in fluoride concentration is indiscernible by eye, but can be readily detected by a photometric instrument. The better the instrument, the better the sensitivity to small increments of fluoride. The acid concentration of the reagent is much higher than that of the visual method, making the reaction virtually instantaneous.

Other Colorimetric Methods

Besides these Standard Methods, many other colorimetric fluoride methods are available. Many of these are designed to eliminate the one-hour waiting period, or at least to shorten it, since this is the principal drawback of the zirconium-alizarin method.

A. The Rubin method is a visual technique which utilizes permanent artificial standards. The color reaction is still that of the zirconium-alizarin method and as such must be carefully timed.

B. The ECR (Eriochrome Cyanine R) photometric method is similar to ths SPADNS method in that it uses a high acid concentration causing the reaction to be almost instantaneous. While the advantages of the reagent, such as speed, sensitivity and tolerance to many interferences make it quite useful, it has two distinct disadvantages. These are its intolerance for sulfate and the requirement for spectrophotometric measurement. The sulfate can be analyzed for separately, and appropriate compensation made, but the extra analytical step greatly increases the possibility of error. The necessity for using a spectrophotometer limits use of the method to laboratories which are equipped with this instrument.

C. The Alizarine Complexone methods use a different color system. Since the color change is from blue to red with increasing amounts of fluoride, the use of a red filter will produce a calibration curve with positive slope. The reaction is not immediate, but slow enough so that fluoride can be measured after a 15-minute waiting period. Other disadvantages are that the reagent is not too stable and tolerance to aluminum is particularly poor.

Photometric vs. Visual Methods

In general, the photometric methods are to be preferred over visual techniques, since their advantages far outweigh their disadvantages.

A. The ability to obtain more accurate analyses, and the virtual elimination of the human element are qualities inherent in an instrumental technique. Furthermore, the reagents available for photometric methods are more sensitive and more stable. The infrequent preparation of a standard curve is a more preferable operation than the preparation of visual standards for each set of samples. With a small amount of manipulation, a photometer can be used to compensate for color and turbidity in the water sample, although distillation is usually preferred in such cases.

B. On the debit side of the ledger, a photometer is admittedly more expensive than is a set of Nessler tubes, although the expense can often be justified by the multiple analyses for which the photometer can be used. Another disadvantage of a photometric method, sometimes applicable to visual methods as well, is that glassware must be scrupulously clean in order to avoid changes in the light transmittance of the sample cell itself.

Sources of Error in Colorimetric Analysis

The analysis of water is a comparatively delicate operation - the quantities involved are minute, and the greatest possible accuracy is desirable. For these reasons, no possible source of error can be overlooked.

A. The reagent, which contains not only the components which form the color lake, but also the acid for achieving the desired pH, must be accurately measured. This implies the correct pipetting technique.

B. Glassware, whether Nessler tubes or photometer cells, must be clean and perfectly matched.

C. When treated water samples are being analyzed, the presence of chlorine must always be suspected, and when necessary, the chlorine eliminated with aresnite. The use of thiosulfate for this purpose should be discouraged, since an excess can produce turbidity in the sample.

D. Although color and turbidity can be compensated for in some cases, it is always best to distill such samples.

E. Analytical results obtained with any of the colorimetric reagents are limited to a very narrow range of fluoride values, and samples which approach or exceed the limit of the range must be appropriately diluted. The dilution must be made before addition of reagent, since subsequent dilution will affect the concentration of dye, zorconium and acid.

F. While exact timing is not important in the visual method, it is imperative that both standards and samples be treated with reagent as nearly simultaneously as possible so that the color development will progress to the same degree in each. In any method, temperature of samples must match standards or the standard curve.

G. Perhaps the most important source of error is the presence of interfering ions in the water sample. It is readily conceded that none of the colorimetric methods is entirely specific for fluoride, and to varying degrees many of the other ions found in water affect the fluoride analysis. The reagents are designed to provide as much tolerance as possible for these interfering ions, but when the limits of tolerance are exceeded or when any doubt exists as to the presence or quantity of such interferences, the water sample must be distilled before an accurate fluoride analysis can be made.

The Electrode Method

The basis for this method is in the fluoride electrode itself. Most electrodes contain a fluoride solution; at the tip of the electrode is a crystal doped with fluoride ions. The crystal acts as an ion-exchange membrane, so that when the fluoride concentration outside of the electrode is higher than that inside, ions move toward the inside setting up a voltage potential proportional to the difference in fluride concentration. Conversely, when the fluoride concentration on the outside is lower than that on the inside, a proportional potential of opposite sign is set up. In most fluoride electrodes, the internal solution is about 10^{-3} molar in fluoride, so concentrations below 19 ppm result in positive voltage readings. Some electrodes contain no internal solution, but the principle of operation is similar. However, in the solid electrodes the potential developed by a particular fluoride solution is independent of a filling solution but rather depends entirely on the characteristics of the particular crystal used in the electrode manufacture.

A. The electrode measures ion activity only, so that fluoride present in un-ionized form will not be detected. At low pH's, when un-ionized HF is present, and in the presence of complexing agents like aluminum, for example, low readings will result. The only known interference is hydroxide ion, but for practical purposes, aluminum and other complexing agents must also be considered as interferences since they affect the formation of fluoride ions.

B. A system has been developed whereby the electrode can be used to detect fluoride concentration instead of fluoride ion activity. The system utilizes a buffer mixture which, when added to the sample, controls the pH, ties up complexing agents and provides a high ionic strength background so that ion activity remains proportional to concentration. When this buffering system is used, most water samples can be read directly without dilution regardless of concentration, and without regard to color, turbidity, etc. The only likely interference is aluminum in relatively high concentration, and even this can be overcome by making a small adjustment to the buffer composition.

References

1. Sanchis, J. M. Determination of Fluorides in Natural Waters. Anal. Chem., 6:134 (1934).

2. Scott, R. D. Modification of the Fluoride Determination. Jour. AWWA, 33:2018 (Nov. 1941).

3. Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, New York (13th ed., 1970).

4. Maier, F. J. Manual of Water Fluoridation Practice, McGraw-Hill, 1963.

5. Bellack, E. and Schouboe, P. J. Rapid Photometric Determination of Fluoride with SPADNS-Zirconium Lake. Anal. Chem. 30:2032 (1958).

6. Bellack, E. Simplified Fluoride Distillation Method. Jour. AWWA, 50:530 (1958).

7. Bellack, E. Automatic Fluoride Distillation, Jour. AWWA, 53:98 (1961).

8. Task Group Report. Study of Permanent Color Comparators for Fluorides. Jour. AWWA, 49:417 (1957).

9. Task Group Report. Further Study of Permanent Color Comparators for Fluoride. Jour. AWWA, 53:989 (1961).

CONTROL OF INTERFERING IONS

I. The principal source of error in fluoride analysis is the presence of interfering ions. This is particularly true in the colorimetric methods, as can be seen from Table I which lists some ions commonly found in water and their affect on the Standard Methods fluoride analyses.

   A. In colorimetric analysis, one of the mechanisms by which these ions cause error is the changing of the reaction rate. Since the determination is based on color development, variations in reaction rate cause variations in fluoride reading.

   B. Some ions complex with either fluoride, in all methods, or with zirconium, in the colorimetric methods. When fluoride is complexed, low results are obtained, and when zirconium is complexed, the intensity of color is altered.

   C. Chlorine bleaches out the colors of dyes, and must always be removed before the sample can be analyzed colorimetrically.

II. Whenever the quantity of interfering ions in the water is sufficient to cause an error of 0.1 ppm fluoride or more, or whenever the analysis is unknown, these interferences must be removed or their effects diminished by one of the following methods:

   A. If the interferences are known to be caused by chemicals added during treatment in the water plant, they may sometimes be avoided by appropriate selection of a sampling point within the plant.

   B. In some cases the water sample can be diluted to bring the level of an interfering ion below the critical point. This procedure is applicable only when the fluoride level is sufficiently high to permit

accurate analysis on the diluted sample.

C. When the identity of the interfering ion is known, it may be possible to select an analytical method which has adequate tolerance for that ion.

TABLE 1 INTERFERENCES

Concentration of Substance, in Mg/L, Required to Cause an Error of Plus or Minus 0.1 Mg/L at 1.0 Mg/L F.

	Scott-Sanchis	SPADNS	Electrode
Alkalinity	400 (-)	5,000 (-)	7,000 (+)
Aluminum	0.25 (-)	0.1 (-)	2.0 (-)
Chloride	2,000 (-)	7,000 (+)	20,000 (-)
Iron	2 (+)	10 (-)	200 (-)
Hexametaphosphate	1.0 (+)	1.0 (+)	50,000
Phosphate	5 (+)	16 (+)	50,000
Sulfate	5 (+)	16 (+)	50,000 (-)
Chlorine	Must be completely removed with Arsenite		5,000
Color & Turbidity	Must be removed or compensated for ----		

D. When the composition of the unfluoridated water is known and constant, equivalent quantities of interfering ions can be added to the fluoride standards, thereby neutralizing the effect of those ions.

E. In all other cases the water sample must be distilled. As can be seen from Table I, distillation will seldom be necessary when the electrode method is used.

III. The principle of the distillation process is the conversion of fluoride to the volatile acid, H_2SiF_6, in the presence of sulfuric acid and silica (glass beads). The fluosilicic acid distills over, leaving most of the interfering ions behind.

A. The apparatus used is illustrated in Figure 1. It consists of a distillation flask, connecting tube and condenser. For convenience, apparatus with ground-glass joints is used, but a simpler arrangement using rubber stoppers is satisfactory (Figure 2).

B. The critical features of the apparatus are the diameter of the connecting tube, the immersion of the thermometer, and fit of stoppers and/or ground-glass joints.

1. The diameter of the connecting tube must be large enough to preclude the carryover of bubbles.
2. The thermometer must be positioned low enough so that it will always be immersed.
3. Stoppers and joints must be tight enough to prevent the loss of fluoride-containing vapor.

C. The distillation procedure is carried out as follows:

1. Prepare the still by placing 400 ml distilled water, some glass beads and then 200 ml concentrated acid in the flask. Add the acid slowly and stir thoroughly. After all the acid has been added, stir again until the mixture is homogeneous.

2. Connect the apparatus as shown in the drawing, start water through the condenser and begin heating slowly. If bumping occurs, the acid and water have not been mixed sufficiently. When boiling starts, heating may be increased.
3. Continue heating until the temperature reaches 180° C. Discard this distillate, since it contains traces of fluoride from the acid and glassware. This preliminary procedure also serves to adjust the acid-water ratio for subsequent distillations.
4. Allow the flask to cool until the temperature drops to 120° C. or lower. Measure out a 300 ml sample and add it to the flask. Mix thoroughly.
5. Distill as before until the temperature reaches 180° C. Retain the distillate (there should be 300 ml) for colorimetric determinations.

D. The distillation process must be carried out very carefully, since there are several possible sources of difficulty.
1. The flame under the distillation flask must never touch the sides of the flask above the liquid level. Superheating of the vapor results in high sulfate carryover which causes a sulfate interference.
2. All stopper and joints must fit tightly to prevent loss of fluoride.
3. Flask contents must be thoroughly mixed to prevent bumping.
4. Distillation must be stopped when the temperature reaches 180° C. Higher temperatures result in excessive sulfate carryover.

5. Silver sulfate, at the ratio of 5 mg/mg of Cl, should be added when high-chloride samples are distilled. The presence of silver inhibits the volatilization of HCl which, in sufficient quantity, could interfere with the fluoride determination.
6. When high-fluoride samples are distilled, repeat the distillation using 300 ml of distilled water. Analysis of the distillate will indicate how complete the fluoride recovery was. If substantial amounts of fluoride appear in the second distillate, and the quantity to that obtained initially and flush again. Quantities of less than 0.1 ppm (F (0.03 mg) may be disregarded.
7. Because of the simplicity of apparatus and procedure, the distillation procedure can be readily automated. Modifications include magnetic stirring and a thermostat which turns off a quartz heating mantle when the correct temperature has been reached.

SPADNS METHOD

Discussion

The reaction rate between fluoride and zirconium ions is influenced greatly by the acidity of the reaction mixture. By increasing the proportion of acid in the reagent, the reaction can be made practically instantaneous. Under such conditions, however, the effect of various ions differs from that in the conventional alizarin methods. The selection of dye for this rapid fluoride method is governed largely by the resulting tolerance to these ions.

Apparatus

Colorimetric equipment: One of the following is required:

a. Spectrophotometer, for use at 570 nm., providing a light path of at least 1 cm.

b. Filter photometer, providing a light path of at least 1 cm. and equipped with a greenish yellow filter having maximum transmittance at 550 to 580 nm.

Reagents

a. Standard fluoride solution: Prepare as directed in the electrode method, Section 414B. 3b.

b. SPADNS Solution: Dissolve 958 mg SPADNS, sodium 2-(para-sulfophenylazo)-1, 8-dihydroxy-2, 6-naphthalene disulfonate, also called 4,5-dihydroxy-3-(parasulfophenylazo)-2,7-naphthalenedisulfonic acid trisodium salt, in distilled water and dilute to 500 ml. This solution is stable indefinitely if protected from direct sunlight.

c. Zirconyl-acid reagent: Dissolve 133 mg zirconyl chloride octahydrate, $ZrOCl_2.8H_2O$, in about 25 ml distilled water. Add 350 ml conc HCl and dilute to 500 ml with distilled water.

d. Acid zirconyl-SPADNS reagent: Mix equal volumes of SPADNS solution and zirconyl-acid reagent. The combined reagent is stable for at least 2 years.

e. Reference solution: Add 10 ml SPADNS solution to 100 ml distilled water. Dilute 7 ml conc HCl to 10 ml and add to the diluted SPADNS solution. The resulting solution, used for setting the reference point (zero) of the spectrophotometer or photometer, is stable and may be reused indefinitely. Alternatively, use one of the prepared standards as a reference.

f. Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ and dilute to 1 l. with distilled water. (Caution: Toxic--Take care to avoid ingestion.)

Procedure

a. Preparation of standard curve: Prepare fluoride standards in the range of 0 to 1.40 mg/l by diluting apprppriate quantities of the standard fluoride solution to 50 ml with distilled water. Pipet 5.00 ml each of SPADNS Solution and zirconyl-acid reagent, or 10.00 ml of the mixed acid zirconyl SPADNS reagent, to each standard and mix well. Avoid contamination during the process. Set the photometer to zero absorbance with the reference solution and obtain the absorbance reading of the standards immediately. Plot a curve of the fluoride-absorbance relationship. Prepare a new standard curve whenever a fresh reagent is made or a different standard temperature is desired. If no reference solution is used, set the photometer at some convenient point established with a

prepared fluoride standard.

b. Sample pretreatment: If the sample contains residual chlorine, remove it by adding 1 drop (0.05 ml) $NaAsO_2$ solution/0.1 mg Cl and mix. (Sodium arsenite concentrations of 1,300 mg/l produce an error of 0.1 mg/l at 1.0 mg/lF.)

c. Color development: Use a 50.0 ml sample or a portion diluted to 50 ml. Adjust the temperature of the sample to that used for the standard curve. Add 5.00 ml each of the SPADNS solution and zirconyl acid reagent, or 10.00 ml of the acid zirconyl acid reagent, or 10.00 ml of the acid zirconyl SPADNS reagent; mix well and read the absorbance immediately or at any subsequent time, first setting the reference point of the photometer as above. If the absorbance falls beyond the range of the standard curve, repeat the procedure, using a smaller sample.

Calculation

$$\text{mg/l F} = \frac{A}{\text{ml sample}} \times \frac{B}{C}$$

Where A = ug F determined photometrically. The ratio B/C applies only when a sample is diluted to a volume B, and a portion C taken from it for color development.

Precision and Accuracy

A synthetic sample containing 830 ug/l F and no interference in distilled water was analyzed in 53 laboratories by the SPADNS method, with a relative standard deviation of 8.0% and a relative error of 1.2%. After direct distillation of the sample, the relative standard deviation was 11.0% and the relative error 2.4%.

A synthetic unknown sample containing 570 ug/l F, 10 mg/l Al, 200 mg/l sulfate, and 300 mg/l total alkalinity was analyzed in 53 laboratories by the SPADNS method without distillation, with a relative standard deviation of 16.2% and a relative error of 7.0%. After direct distillation of the sample the relative standard deviation was 17.2% and the relative error 5.3%.

A synthetic unknown sample containing 680 ug/l F, 2 mg/l Al, 2.5 mg/l sodium hexametaphosphate, 200 mg/l sulfate, and 300 mg/l total alkalinity was analyzed in 53 laboratories by direct distillation and SPADNS methods with a relative standard deviation of 2.8% and a relative error of 5.9%.

FLUORIDE

(Electrode)

STORET NO: Total 00951

Dissolved 00950

1. Scope and Application

   1.1 This method is applicable to the measurement of fluoride in drinking, surface, and saline waters, domestic and industrial wastes.

   1.2 Concentration of fluoride from 0.1 up to 1000 mg/liter may be measured.

   1.3 For Total or Total Dissolved Fluoride, the Bellack distillation must be performed on the samples prior to electrode analysis.

2. Summary of Method

   2.1 The fluoride is determined potentiometrically using a selective ion fluoride electrode in conjunction with a standard single junction sleeve-type reference electrode and a pH meter having an expanded millivolt scale or a selective ion meter having a direct concentration scale for fluoride.

   2.2 The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions. The cell may be represented by Ag/AgCl, Cl^- (0.3), F^- (0.001 LaF/test solution/ SCE/.

3. Interferences

   3.1 Extremes of pH interfere; sample pH should be between 5 and 9. Polyvalent cations of Si^{+4}, Fe^{+3} and Al^{+3} interfere by forming

complexes with fluoride. The degree of interference depends upon the complexing cations, the concentration of fluoride and the pH of the sample. The addition of a pH 5.0 buffer (described below) containing a strong, chelating agent preferentially complexes aluminum (the most common interference), silicon, and iron and eliminates the pH problem.

4. Sampling Handling and Preservation

   4.1 No special requirements

5. Apparatus

   5.1 Electrometer (pH meter), with expanded mv scale, or a selective ion meter such as the Orion 400 Series.

   5.2 Fluoride Ion Activity Electrode, such as Orion No. 94-09(1)

   5.3 Reference electrode, single junction, sleeve type, such as Orion No. 90-01, Beckman No. 40454, or Corning No. 476010.

   5.4 Magnetic Mixer, Teflon-coated stirring bar.

6. Reagents

   6.1 Buffer solution, pH 5.0-5.5: To approximately 500 ml of distilled water in a 1 liter beaker add 57 ml of glacial acetic acid, 58 g of sodium chloride and 2 g of CDTA(2). Stir to dissolve and cool to room temperature. Adjust pH of solution to between 5.0 and 5.5 with 5 N sodium hydroxide (about 150 ml will be required). Transfer solution to a 1 liter volumetric flask and dilute to the mark with distilled water. For work with brines, additional NaCl should be added to raise the chloride level to twice the highest expected level of chloride in the sample.

6.2 Sodium fluoride, stock solution: 1.0 ml = 0.1 mg F. Dissolve 0.2210 g of sodium fluoride in distilled water and dilute to 1 liter in a volumetric flask. Store in chemical-resistant glass or polyethylene.

6.3 Sodium fluoride, standard solution: 1.0 ml = 0.01 mg F. Dilute 100.0 ml of sodium fluoride stock solution (6.2) to 1000 ml with distilled water.

7. Calibration

7.1 Prepare a series of standards using the fluoride standard solution (6.3) in the range of 0 to 2.00 mg/l by diluting appropriate volumes to 50.0 ml. The following series may be used:

Milimeters of Standard (1.0 ml = 0.01 mg/F)	Concentration when Diluted to 50 ml, mg F/liter
0.00	0.00
1.00	0.20
2.00	0.40
3.00	0.60
4.00	0.80
5.00	1.00
6.00	1.20
8.00	2.60
10.00	2.00

7.2 Calibration of Electrometer: Proceed as described in (8.1). Using semilogarithmic graph paper, plot the concentration of fluoride in mg/liter on the log axis vs. the electrode potential developed in the standard on the linear axis, starting with the lowest concentration

at the bottom of the scale. Calibration of a selective ion meter: Follow the directions of the manufacturer for the operation of the instrument.

8. Procedure

8.1 Place 50.0 ml of sample or standard solution and 50.0 ml of buffer (See Note) in a 150 ml beaker. Place on a magnetic stirrer and mix at medium speed. Immerse the electrodes in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 mg/liter F, it may require as long as five minutes to reach a stable meter reading; higher concentrations stabilize more quickly. If a pH meter is used, record the potential measurement for each unknown sample and convert the potential reading to the fluoride ion concentration of the unknown using the standard curve. If a selective ion meter is used, read the fluoride level in the unknown sample directly in mg/l on the fluoride scale.

NOTE: For industrial waste samples, this amount of buffer may not be adequate. Analyst should check pH first. If highly basic (11), add 1 N HCl to adjust pH to 8.3.

9. Precision and Accuracy

9.1 A synthetic sample prepared by the Analytical Reference Service, PHS, containing 0.85 mg/l fluoride and no interferences was analyzed by 111 analysts; a mean of 0.84 mg/l with a standard deviation of ± 0.03 was obtained.

9.2 On the same study a synthetic sample containing 0.75 mg/l fluoride, 2.5 mg/l polyphosphate and 300 mg/l alkalinity, was analyzed by the

same 111 analysts; a mean of 0.75 mg/l fluoride with a standard deviation of ± 0.036 was obtained.

Bibliography

1. Patent No. 3,431,182 (March 4, 1969).
2. CDTA is the abbreviated designation of 1, 2-cyclohexylene dinitrilo tetraacetic acid, (Mathieson, Coleman & Bell, Cat. No. P8661) or cyclohexane diamine tetraacetic acid (Merck-Titriplex IV or Baker Cat. No. G083).
3. Standard Methods for the Examination of Water and Wastewaters, p. 171, Method No. 121A, Preliminary Distillation Step (Bellack), 13th Edition, 1971.

Fig. 1 DISTILLATION APPARATUS